Headspace Analysis of Engine Oil by Gas Chromatography/Mass Spectrometry

Dianne M. Levermore, Mira Josowicz, William S. Rees, Jr., and Jiří Janata*

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

This study establishes the rationale necessary for determining the time to change engine oil. This is based on identifying gaseous components in new and used automobile lubricants. Key compounds, so-called "signature", are separated and identified qualitatively by coupled gas chromatography/mass spectrometry. Volatile antioxidants at zero miles and fuel contaminants at low mileage are observed in the headspace of engine oil. Several oxidative degradation components have been positively identified in the used oil, which include the following: acetaldehyde, acetone, butanal, 2-propanol, acetic acid, 2-hexanol, benzoic acid, benzaldehyde, and 1-pentanol. This study strongly suggests that the status of lubricating oil can be determined by the analysis of the gas phase above the oil. Most importantly, it opens the possibility of performing conditional maintenance of the combustion engine based on information obtained from gas sensors.

Frequent oil changes (less than 7500 miles) are a poor choice both economically and environmentally; however, infrequent oil changes (greater than 7500 miles) may lead to engine damage. The lube manufacturers recommended interval is every 3000 miles or 3 months. Automobile manufacturers recommend every 7500 miles.[1] Frequent and unnecessary oil changes can be costly to the consumer, (operators of passenger cars, fleet transport, industrial combustion engines, and military machinery), with a portion of that cost going toward disposal of the used engine oil. Conversely, infrequent oil changes may lead to premature engine wear, hence the need for a costly overhaul. The correct drain period of an automobile's engine oil is unknown; therefore, there is a need to determine when the useful life of the oil will expire. A rational decision based on chemical analysis would be a preferable option. A phrase "conditional maintenance" has been coined for this approach.

There are three reasons for engine oil deterioration: contamination, depletion of additives, and oxidation.[2] Depletion of additives usually precedes the formation of oxidation products and is accelerated by the presence of contaminants. This complex degradation process depends on the mechanical status and operating conditions of the engine. Consequently, there is a need for conditional maintenance of engine oil and a rational approach to discriminate between good/new oil and bad/used oil.

Fuel, soot, water, and ethylene glycol are common contaminants that may be found in the oil. The presence of unburned fuel indicates that there is an incorrect fuel/air ratio resulting in poor combustion. Often this will reduce oil viscosity, depress the flashpoint, and accelerate oxidation of the engine oil. Water and soot are products of combustion; however, if present in excess, they can increase the oil viscosity and forewarn of engine malfunction.[2] Ethylene glycol is the main ingredient of antifreeze, and detection of it in engine oils is an indicator of engine failure.[3]

Additive depletion usually occurs as a result of the presence of contaminants and the formation of oxidation products. The use of antioxidants inhibits oxidative degradation and usually consists of (a) radical scavengers, (b) hydroperoxide decomposers, or (c) synergistic mixtures of both types of antioxidants.[4] As the oil ages, the antioxidants, which are alkaline in nature, are neutralized by the acidic oxidation products. Once all the antioxidants have been used up the oil begins to accumulate corrosive acids that etch the metal parts causing further damage to the engine.

Engine oil oxidizes in service as it flows through the engine in the presence of dissolved oxygen and contaminants at temperatures that at some locations exceed 260 °C.[5] The hydrocarbons undergo autoxidation, a self-accelerating oxidation process involving radical chain reactions catalyzed by trace metals. Peroxides are formed initially, followed by aldehydes, ketones, carboxylic acids, alcohols, and esters as final oxidation products. The presence of any of these compounds in the lubricant is an important indicator of the remaining degree of oil serviceability. These low molecular weight (LMW) compounds can further condense and polymerize to give high molecular weight compounds (HMW) that consist of sludge, polymers, and solid particulate.[6] The low molecular weight compounds also contain volatile hydrocarbon fragments, CO_2, CO, and highly volatile unsaturated hydrocarbons.[4] The presence of both the LMW and HMW compounds degrades the performance of the engine oil and monitoring them can indicate the condition of the oil and the engine.

A substantial amount of research has been done on the liquid properties of engine oil. Much of this work involves measuring and determining the dispersivity, viscosity, total base number (TBN), total acid number (TAN), insoluble content, molecular

* Corresponding author: (phone) (404) 894 4828; (fax) (404) 894 8146; (e-mail) jiri.janata@chemistry.gatech.edu.
(1) Toyota Tercel owner's manual, 1995.
(2) Heron, B. *Mar. Eng. Rev.* 1986, 23–25.

(3) Smolenski, D. J.; Schwartz. S. E. *Lubr. Eng.* 1994, 50, 9, 716–722.
(4) Mortier, R. M.; Orszulik, S. T. *Chemistry and Technology of Lubricants,* 2nd ed., Blackie Academic & Professional: London, U.K., 1997; p 109.
(5) Kaleli, H.; Yavasliol, I. *Ind. Lubr. Tribol.* 1997, 49 (3), 120–126.
(6) Naidu, S. K.; Klaus, E. E.; Duda, J. L. *Ind. Eng. Chem. Prod. Res. Dev.* 1984, 23, 613–619.

structure (chemical identification by IR), and metal wear (elemental analysis, emission spectrograph, atomic absorption, and X-ray absorption) of the oil.[7,8] GC and GC/MS have also been used as a means to separate, identify, and quantify oxidation products[9,10] and contaminants[11] that make their way into the lubricant as the engine oil degrades. Additionally, there is an abundance of literature available on the oxidation of engine oils in the attempt to determine individual carboxylic acids and aldehydes. These studies involved complicated sample preparation and pretreatment of the oil that included adding and removing several compounds.[12-15]

Through proper sample preparation, interfering components can be removed and the GC/MS can separate and detect compounds of similar structures present at low levels in the complex matrix. Since most compounds have a measurable vapor pressure and their solubility in liquid decreases with increasing temperature, headspace sampling is an ideal technique for sample introduction into the GC.[16] The volatile components can equilibrate by partitioning between the sample (solid/liquid) and the gas phase.[17] Since engine oil basestocks are composed of a complex mixture of linear and branched alkyl substituents with various functional groups, headspace sampling can provide a true, homogeneous, and simple matrix for analyte separation and compound identification.

To date there is little information available on the individual degradation products of engine oil in either the liquid or the gas phase. Maleville et al. provides a list of the volatile degradation products caused by the laboratory oxidation of mineral-based oil.[9] The present work will identify the principal gaseous components of the new and used engine oil in service and establish the concept of oil condition monitoring via the vapor phase.[18]

EXPERIMENTAL SECTION

Chemicals. Acetaldehyde, acetic acid, acetone, benzaldehyde, benzoic acid, butanal, 2-propanol, 1-pentanol, 2-hexanol, naphthalene, and toluene were from Aldrich Chemical Co. (Milwaukee, WI). A mixture containing all the compounds was prepared and used as a standard. All glassware was cleaned and baked in an oven at 150 °C overnight.

Oil Samples. 10W-30 is the most commonly used viscosity grade for automobile engines and was chosen for use in this study for proof of concept. New engine oil samples (Car and Driver 10W-30, Pennzoil 10W-30, Valvoline 10W-30, Castrol GTX 10W-30, and

(7) Asseff, P. A. *SAE Tech. Pap.* **1977**, No. 770642, 1−11.
(8) Picken, D. J.; Seare, K. D. R.; Thompson, A. L.; Fox, M. F.; Preston, W. H. *IMechE Semin. Pub.* **1991**, 115−120.
(9) Maleville, X.; Faure, D.; Legros, A.; Hipeaux, J. C. *Lubr. Sci.* **1996**, *9* (1), 3−60.
(10) Kawamura, K.; Ng, L.; Kaplan I. R. *Environ. Sci. Technol.* **1985**, *19*, 1082−1086.
(11) Hiltz, J. A.; Haggett, R. D. *Lubr. Eng.* **1991**, *47* (11), 945−955.
(12) Lewis, S. W.; Worsford, P. J.; Lynes, A.; McKerrell, E. H. *Anal. Chim. Acta* **1992**, *266*, 257−264.
(13) Gachanja, A. N.; Worsford, P. J. *Anal. Chim. Acta* **1994**, *290*, 226−232.
(14) Lewis, S. W.; Worsford, P. J.; McKerrell, E. H. *J. Chromatogr., A* **1994**, *667*, 91−98.
(15) Gachanja, A. N.; Lewis, S. W.; Worsford, P. J., *J. Chromatogr., A* **1995**, *704*, 329−337.
(16) Cowper, C. J.; DeRose, A. J. *The Analysis of Gases by Chromatography*, Pergamon Press: Oxford, England, 1983; pp 103−111.
(17) McNair, H.; Miller, J., *Basic Gas Chromatography*; John Wiley & Sons: New York, 1998; pp 164−165.
(18) Janata, J. U.S. Patent 6,128, 561, 2000.

Mobil 10W-30) were purchased from a local superstore. Used oil samples were aged and collected from a passenger car (gasoline powered, 1996 Toyota Tercel, ~90 000 miles), which consistently used Pennzoil 10W-30 as its engine lubricant. Oil samples were removed from the car at 235, 4080, 7256, and 8376 miles.

Sample Handling. A 500-μL gastight syringe (Hamilton Co., Reno, NV) was initially used as a means of sample introduction. The syringe was later replaced with solid-phase microextraction (SPME) in order to eliminate sample handling/sample transfer losses. It was determined that both techniques gave similar results; however, the SPME was retained and used in later experiments.

Solid-phase microextraction holder and fiber assemblies for manual extraction were obtained from Supelco Inc. (Bellefonte, PA). Four of the fiber types were compared, which included stationary-phase coatings of poly(dimethylsiloxane) (PDMS; 100 μm), poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB; 65 μm), Carboxen/poly(dimethylsiloxane) (CAR/PDMS; 75 μm), and Carbowax/divinylbenzene (CW/DVB; 65 μm). The fibers were conditioned by baking in the gas chromatograph (GC) injection port for the recommended temperature and time. Additionally, blank analysis was carried out to check for contamination.

Instrumentation. Analysis was carried out using a Hewlett-Packard (Palo Alto, CA) HP 5890 Series II Plus capillary gas chromatograph coupled with an HP 5972 mass spectrometer via a heated transfer capillary line (280 °C). Injections into the GC were made in the split mode with a split ratio of 100:1 and an injector temperature of 280 °C. Helium was used as the carrier gas with a constant flow rate of 0.8 mL/min. The columns used were HP-INOWAX (cross-linked PEG) 60 m × 0.25 mm i.d. column (d_f = 0.25 μm), (linear velocity 22.8 cm/s, 12.9 psi at 40 °C) and HP-5 (5% phenyl methyl silicone) 30 m × 0.25 mm i.d. column (d_f = 0.25 μm), (linear velocity 32.2 cm/s, 4.8 psi at 40 °C).

For experiments performed using the HP-INOWAX column, the GC temperature program consisted of a 3-min hold at 40 °C, a ramp at 10 °C/min up to 150 °C, and then a hold at 150 °C for 9 min (23 min total run time). Other experiments employed the HP-5 column with a temperature program consisting of holding the column at 40 °C for 3 min, ramping the temperature to 150 °C at a rate of 10 °C/min, and finally holding the column at 300 °C for 9 min. The program took 38 min to complete.

The mass spectrometer was operated either in the full-scan mode or in the selected ion monitoring (SIM) mode. In the full-scan mode, a mass range of 50−550 atomic mass units was chosen at a rate of 1.53 scans/s. M/z values of 105 and 122 were used for SIM mass detection of benzoic acid. The instrument was tuned prior to analysis and calibrated with perfluorotributylamine (PFTBA). Identification of the unknown in the samples was carried out by the following: (a) comparison of their spectra with the Wiley National Bureau Standards library of mass spectral data and (b) comparison of their chromatographic retention times with standards.

Analytical Setup and Procedure. A simple setup was designed for acquiring samples in the laboratory. The experimental apparatus consisted of a thermometer, an air-cooled condenser, a three-neck flask, a thermostatically controlled heater, and a stirrer. A vapor was generated when the oil was heated at 6 °C/min to 140 °C in air. Extraction of the headspace was performed
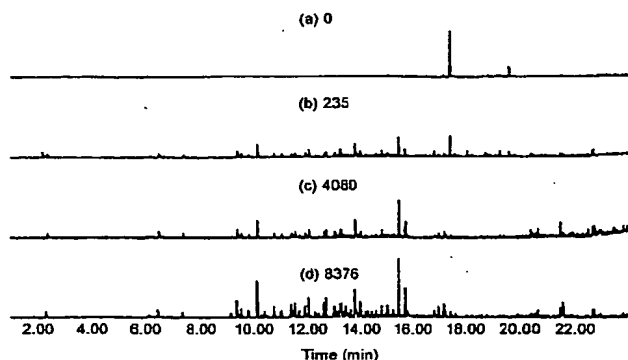
Figure 1. Total ion chromatogram of engine oil collected at (a) 0, (b) 235, (c) 4080, and (d) 8376 miles and sampled in the headspace by SPME at 140 °C.

using a 500-μL Hamilton gastight syringe, and oil samples were introduced into the GC. The oil was allowed to cool, and additional samples were taken at 105, 70, and 35 °C.
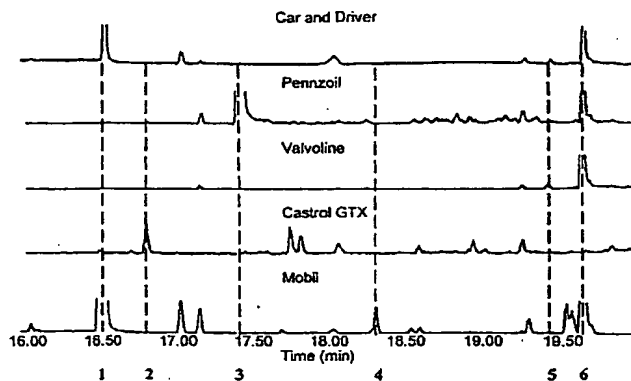
For SPME sampling, the oil was heated at 9.33 °C/min in air to 140 °C and allowed to equilibrate at that temperature for 10 min. The SPME fiber was exposed to the headspace of the oil samples for 2 min. During fiber exposure, the oil was stirred. The fiber was retracted and the holder was removed and rapidly transferred to the GC/MS where the sample was desorbed for 2 min at 270 °C. The oil was allowed to cool and additional samples were taken at 105, 70, and 35 °C.

RESULTS AND DISCUSSION

Profile of Oil Degradation. Figure 1 shows the total ion chromatogram of engine oils sampled in the headspace at 140 °C at (a) 0, (b) 235, (c) 4080, and (d) 8376 miles. A quick survey of Figure 1 reveals that there is a difference in the condition of the oil at the different miles that correlates with the deterioration of the engine oil in service. Furthermore, the chromatograms confirm that information can be obtained from the headspace about the contents of the engine oil. There is a visible difference between the profiles of the new oil (Figure 1a) and the used oils (Figure 1b–d). Figure 1a shows two prominent peaks at 17.413 and 19.636 min, which indicate the presence of antioxidants in the new oil at the "simulated" engine oil operating temperature of 140 °C. [19] As the new oil is cycled through the engine, from the sump into the cylinder and back into the sump, it becomes tainted with fuel products. This contamination occurs even during the very first operation of the engine following an oil change (Figure 1b). The unburned fuel and/or residues left over from the previous oil change are obviously not indicators of the need to change the oil.

There is a noticeable decrease in the peaks at 17.413 and 19.636 min, indicating depletion of the antioxidants. By the time the oil reaches 4080 miles, as depicted in Figure 1c, all the antioxidants have been consumed and new peaks begin to appear. These new peaks are characteristic of degradation products indicating that the engine oil is reaching the end of its useful lifetime. The profiles of Figure 1c and d only differ in the concentration of degradation products with (d) showing increases in the peak heights. The three principal modes of engine oil degradation are discussed below.

(19) Smolenski, D. J.; Bergin, S. P. *SAE Tech. Pap. Ser.* 1988, No. 881576,

Figure 2. Total ion chromatogram of five different brands of virgin engine oils indicating the presence of common antioxidants (1–6) in the vapor phase.

no.	retention time [min]	compound	bp (°C)
1	16.515	n-butyl benzoate	249
2	16.794	4-tert-amylphenol	255
3	17.413	2,6-di-tert-butylphenol	253
4	18.311	2,6-di-tert-butyl-4-methylphenol	265
5	19.411	2,4,6-tri-tert-butylphenol	277
6	19.636	diphenylamine	302

Contamination. Engine blowby in the form of unburned fuel, fuel combustion products, and airborne dirt finds its way into the oil sump. These fuel components may react with the antioxidants, resulting in their premature depletion. The compounds identified in the headspace gas chromatography analysis by SPME at 235 miles and 140 °C are listed (Table 1). Analysis by mass spectrometry produced numerous peaks of which 66 were identified with varying degrees of certainty from their electron ionization mass spectra (Figure 1b). Table 1 clearly shows the extent of contamination of a fairly new oil sample and represents the order of elution of the different gasoline diluents on an HP-5 column. The first and third columns report the retention times of the identified peaks, while the second and fourth columns represent the identification of the compound achieved by comparison of reference substances contained in the library with the mass spectrometric fragmentation. The aliphatics and aromatics are consistent with the presence of unburned fuel dissolved into the oil. [20] The residuum of the old oil after the oil change falls also into the category of contamination.

Additive Depletion. The purpose of the additives in the engine oil is to enhance its quality and performance and to prolong its useful life. The role of antioxidants is to minimize oxidation and to prevent and control varnish and sludge formation. The depletion of these additives during engine operation can be seen as a form of "titration". [21] In that sense, the conditional maintenance becomes a task of determining the "end point" in this titration.

(20) Ichikawa, M.; Nonaka, N.; Nomura, M.; Takada, I.; Ishimori, S. *J. Anal. Appl. Pyrolysis* 1995, 32, 233–242.

retention time (min)	compound	retention time (min)	compound
0.99	2-pentene, 2-methyl-	13.45	benzene, diethylmethyl-
3.08	pentane, 2,3,4-trimethyl-	13.54	benzene, 1-ethyl-4-(1-methylethyl)-
3.19	hexane, 2,3,4-trimethyl-	13.65	benzene, 1-ethyl-2, 4-dimethyl-
3.55	toluene	13.81	naphthalene
6.88	ethylbenzene	13.96	benzene, (2-methyl-1-butenyl)-
7.12	p-xylene	14.01	dodecane
7.81	benzene, 1,3-dimethyl-	14.21	benzene, (1,1-dimethylethyl) methyl-
8.07	heptane, 2,4-dimethyl-	14.45	benzene, 1-methyl-2-(1-ethylpropyl)-
9.42	benzene, propyl-	14.60	benzene, 1-pentenyl
9.61	benzene, 1-ethyl-4-methyl-	14.82	1H-indene, 2,3-dihydro-4, 7-dimethyl-
9.76	benzene, 1,3,5-trimethyl-	14.89	naphthalene, 1,2-dihydro-6-methyl-
9.85	nonane, 3-methyl-	14.94	decane, 2,3,5-trimethyl-
10.02	benzene, 1-ethyl-2-methyl-	15.03	benzene, (3-methyl-2-butenyl)-
10.31	benzene, 1,2,3-trimethyl-	15.27	benzene, pentamethyl-
10.92	benzene, 1,2,4-trimethyl-	15.36	1H-indene, 2,3-dihydro-1, 1,5-trimethyl-
11.18	benzene, 2-propenyl-	15.48	naphthalene, 1-methyl-
11.50	benzene, 1-methyl-3-propyl-	15.73	naphthalene, 2-methyl-
11.58	benzene, diethyl-	16.11	naphthalene, 1,2,3,4-tetrahydro-1, 4-dimethyl-
11.63	benzene, 1-methyl-2-(1-methylethyl)-	16.16	triacontane
11.73	decane, 2-methyl-	16.51	dodecane, 2,6,11-trimethyl-
11.79	benzene, 1-methyl-2-propyl-	16.66	biphenyl
11.84	decane, 3-methyl-	16.81	tetradecane
11.98	benzene, 2-ethyl-1,3-dimethyl-	16.86	naphthalene, 1-ethyl-
12.13	benzene, 1,2,4,5-tetramethyl	17.00	naphthalene, 2,7-dimethyl-
12.25	benzene, 4-ethyl-1,2-dimethyl-	17.20	naphthalene, 1,7-dimethyl-
12.37	undecane	17.24	naphthalene, 2,6-dimethyl-
12.41	benzene, (1,2-dimethylpropyl)-	17.43	phenol, 2,6-bis(1,1-dimethylethyl)-
12.50	benzene, 2-ethyl-1,4-dimethyl-	17.61	nonacosane
12.66	benzene, 1-ethyl-2,3-dimethyl-	18.07	pentadecane
12.74	benzene, 1,2,3,5-tetramethyl-	18.27	naphthalene, 1,4,6-trimethyl-
13.07	1H-indene, 2,3-dihydro-5-methyl-	18.84	naphthalene, 1,3,6-trimethyl-
13.16	benzene, 1-ethyl-3,5-dimethyl-	19.27	heneicosane
13.25	1H-indene, 2,3-dihydro-4-methyl-	19.65	diphenylamine

The total ion chromatogram showing the presence of antioxidant in five different brands of engine oils is depicted in Figure 2. The profile of the oils at zero miles includes SPME headspace sampling at 140 °C of Car and Driver 10W-30, Pennzoil 10W-30, Valvoline 10W-30, Castrol GTX 10W-30, and Mobil 10W-30. Common antioxidants used in the manufacturing of engine oils include (a) hydroperoxide decomposers, (b) sterically hindered phenols (c) aromatic amines, and (d) organocopper antioxidants. GC/MS has identified (b) and (c) in the headspace of the new oil and is able to monitor its depletion over time as shown in Figure 1a and b. At a retention time of 17.413 min, 2,6-di-tert-butylphenol was identified in the Pennzoil brand of motor oil in a significantly higher abundance than the other additive; likewise, a small amount was found in the Mobil oil. Conversely, 2,6-di-tert-butyl-4-methylphenol (18.311 min) appeared in only the Mobil while 2,4,6-tri-tert-butylphenol was seen in both the Car and Driver and the Valvoline brands at 19.411 min in very small concentrations. Diphenylamine eluted at 19.636 min and was present in four of the five oils, indicating that this antioxidant may be the radical scavenger of choice for most engine oil manufacturers. Compounds found at 16.515 (n-butyl benzoate) and 16.794 min (4-tert-amylphenol) cannot be rationalized on the basis of the available literature. All the antioxidants identified possess boiling points in the temperature range of 249–302 °C.

Castrol GTX represented the anomaly with none of the common antioxidants present in the samples. However, there is

(21) Korcek, S.; Mahoney, L. R.; Johnson, M. D.; Hoffman, S. SAE Trans. 1978, No. 780955.

the possibility that other additives in the form of hydroperoxide decomposers and radical scavengers may be present and were not quantifiable by the mass spectrometer within the GC temperature range. In principle, if the presence of antioxidants could be detected then, the depletion of the antioxidants in service could serve as the detection of the "end point". The problem with this approach is, however, that different brands of oil use different antioxidants, which would complicate the design of the detection scheme. We would like to stress that this study focuses on proving the concept that information can be obtained from the vapor phase of lubricants. It is not a judgment on the quality and/or the performance of different brands of engine oils.

Oxidative Degradation. The conditions required for the oxidation of engine oils involve the presence of metals, harsh operating temperatures, and solubility of oxygen in the oil. When all these parameters are present, the oil can degrade by (a) decomposing to give LMW compounds that are boiled off by the high operating temperatures of the engine or (b) by polymerizing or condensing to produce HMW insolubles that inherently change the viscosity of the lubricant and form sludge and deposits in the engine. Several GC sampling techniques and MS methods were used in order to obtain information on the oxidation products formed as a result of degradation. Identification proved challenging since the oxidation products are present in much smaller concentrations than the other components and contaminants in the engine oil. For that reason, a variety of compounds were followed over a broad range of boiling points. Table 2 lists some oxidative degradation products that were observed in the head-

Table 2. Some Oxidative Degradation Products of Used Engine Oil Observed in Samples over 4080 Miles

no.	compound	boiling point (°C)	$M_r{}^a$	notes
1	acetaldehyde	21	44	b, d, g
2	acetone	56	58	b, d, g
3	butanal	75	72	b, d, g
4	2-propanol	82	60	b, d, g
5	acetic acid	116—117	60	b, d, g
6	2-hexanol	136	102	b, d, g
7	1-pentanol	136—138	88	b, d, g
8	benzaldehyde	178—179	106	b, e, f, g
9	benzoic acid	249	122	c, e, f

^{a} Lists the relative molecular mass (M_r) with each corresponding compound. ^{b} Scan mode. ^{c} SIM mode. ^{d} Syringe sampling. ^{e} SPME sampling technique. ^{f} The nonpolar column. ^{g} The polar column.

space of engine oil at 4080 miles and greater. These compounds appear within the operating temperature of the lubricant.

Vapor Pressures. The vapor pressures of the oxidation products shown in Figure 3 illustrate the behavior of the compounds under normal operating engine temperatures. At the operating pressure of 1 atm (dashed line), the vapor pressures of the low boiling point compounds intersect the line between 21 and 140 °C represented by (a). As depicted in Figure 3, these temperatures are within the normal operating temperatures of the oil in the sump of an automobile's engine (ambient to 140 °C). It is also evident that the vapor pressure of the analyte at 1 atm is also equivalent to its boiling point. This can be seen in the example of water, which has a boiling point of 100 °C. The vapor pressures were obtained from known literature values[22,23] and plotted to confirm the presence of the oxidation products in engine oil. This plot confirms that the compounds should be identifiable in the vapor phase above the engine oil.

(22) Boublik, T.; Fried, V.; Hála, E.. *The Vapour Pressures of Pure Substances: selected values of the temperature dependence of the vapour pressures of some pure substances in the normal and low-pressure region*, 2nd rev. ed.; Physical Science Data 17; Elsevier Science Pub. Co.: Amsterdam, 1984.
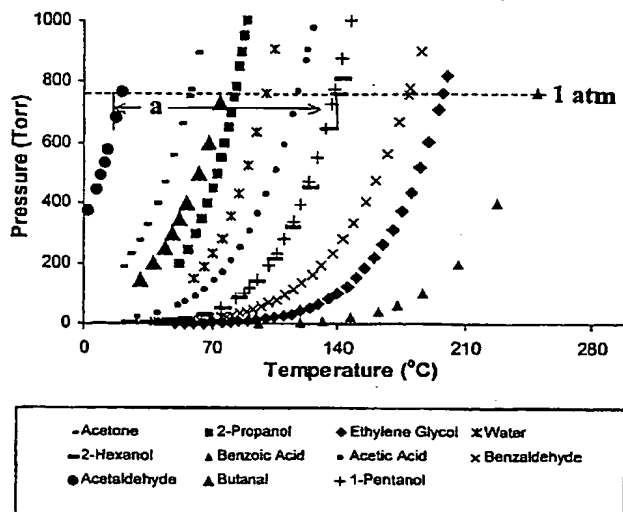(23) Stull, D. *Ind. Eng. Chem.* **1947**, *39*, 525, 526.

Figure 3. Vapor pressures of oxidation products identified in the used oils, water, and ethylene glycol.

CONCLUSIONS

It can be concluded from this study that the vapor phase above engine oil contains the information required to make an informed decision about the time to change the oil. This is not surprising because it is a consequence of the equilibrium between the volatile components in the liquid and gas phases that applies even under the thermodynamically nonideal conditions existing in the combustion engine. This realization opens a new possibility for performing conditional maintenance based on information obtained from gas chemical sensors.